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JAN 79 T H NGUYEN, R T FOLEY

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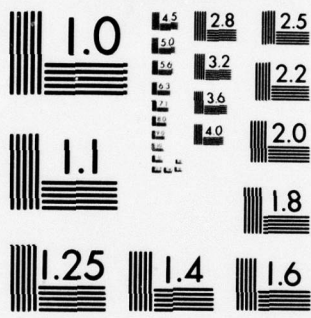
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the literature. The trend toward a decrease in the kinetic order of the pitting reaction with an increase in the pH value of the aggressive solution has been confirmed. The independency of the kinetic order on the electrode potential of the solution indicates that the pitting initiation is controlled by a chemical process with the formation of an intermediate complex and therefore is consistent with the "complex ion theory" of corrosion.

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## ON THE MECHANISM OF PITTING OF ALUMINUM

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The need for a better understanding of the mechanism of the breakdown of passivating oxide films on metals has become more and more apparent. It has been generally accepted that the film formed on the surface of the metal plays an important role in passivity. In practice, the corrosion behavior of aluminum is determined in large part by the behavior of the oxide-covered metal surface towards the corroding media (1). Thus much effort has been expended by means of electrochemical, chemical, optical and electron diffraction methods, in order to correlate film composition (2,3), structure (4) and film thickness (5) of the oxide film with pitting behavior. Lorking (6,7) has emphasized that the corrosion of aluminum is very dependent on the nature of the anion in solution.

There is, at this time, no general agreement with respect to the mechanism by which an oxide film loses its protective character but the extensive and methodical treatment of the uniform corrosion and pitting corrosion of aluminum by Videm (8) should be noted.

Engell and Stolica (9) devised a very simple and useful technique for the study of the breakdown of passivity of iron. Later, this technique was successfully used by Hoar and Jacob (10) for the study of stainless steel and also by Bogar and Foley (11), Foroulis and Thubrikar (12) and Dallek and Foley (13) for pitting on aluminum alloys.

This technique involves potentiostating the metal (electrode) sample in the passive range, injecting a known concentration of an aggressive anion, and measuring the induction time, the time required for a sharp rise in the anodic current to occur. A relationship between the induction time and the concentration of aggressive anion allows an estimation of "n", the number of anions associated with a single surface site during the primary pitting process (13).

Broli and Holtan (14) examined various potentiokinetic methods for determining the characteristic potentials for the pitting of aluminum. They found that the values obtained for the pitting potential,  $E_p$ , and the protection potential,  $E_{pp}$ , and even the existence of two distinct potentials, was dependent on the scan rate used in the measurement. They concluded that only a "stationary" potentiokinetic method (such as the Engell-Stolica method) gave reliable results.

The problem of lack of reproducibility has been encountered by everyone who has worked on the pitting corrosion of metals. Videm (8) circumvented the problem by screening his samples with an electrical test which involved measuring the leakage current through the oxide film in sodium borate solution. Specimens that gave a high and unstable leakage current were rejected. Specimens that gave a low and stable current were classified "normal" and used for pitting initiation tests. In view of the fact that we do not know the reason for such electrical behavior it was decided to use all of the measurements and treat the results statistically.

Due to the statistical nature of the pitting process, the scatter of the induction times measured by the Engell-Stolica technique has

proven to be a major deterrent to the complete utilization of the data obtained. Sato (15) and Shibata (16) have responded to this question by applying the theory of the Markov process to potentiostatic pit generation on a rotating stainless steel electrode but their particular application of the Markov statistic does not seem to be appropriate for the study of pit initiation in general. Accordingly, in this paper we consider the most suitable treatment of the pit initiation data in order to get a meaningful interpretation with this technique.

A second point in the application of the technique deals with the potential at which the sample is potentiostated. In the Engell and Stolice technique the metal electrode is held potentiostatically in the passive range in an appropriate electrolyte for a specific time before injection of the aggressive anion solution. The understanding of the effect of the applied potential is necessary for the interpretation of the pitting mechanism. Thus, one objective of this investigation was to measure the variation of the induction time,  $\tau$ , as a function of the potential applied in the passive range. The potential dependence or independence would suggest an electrochemical or chemical rate determining rate process.

It had been previously established (11, 13) that the stoichiometric number, "n", that is, the number of halide ions associated with an aluminum site in the primary pit initiation reaction is high in solutions of low pH. Species such as  $\text{Al}_2\text{Cl}_6$  and  $\text{AlBr}_4$  were postulated. In nearly neutral solutions the "n" value was low suggesting species such as  $\text{Al}(\text{OH})_2(\text{Cl})_2^-$  and  $\text{Al}(\text{OH})_2(\text{Br})_2^-$ . It was desirable to establish the stoichiometric number at intermediate pH's to learn whether or not an actual trend in "n" values existed.

## Experimental

The experimental technique is described in detail in previous publications (11, 13). The experiments were conducted in an electrolytic cell containing a specially designed Teflon electrode holder, a  $\text{Hg}/\text{Hg}_2\text{SO}_4$  reference electrode, a Luggin capillary and a counter electrode which was separated from the rest of the cell by a fine porosity glass frit. Stirring was provided by a submersible water-powered magnetic stirrer. The cell was thermostated with a refrigerated and heated water bath. The potential of the working electrode was controlled by an Anotrol Model 4100 research potential controller; a Keithley Model 600A electrometer was used for the more accurate measurement of the potential of the working electrode. The current was recorded on a Sargent Model SRL recorder and displayed by a Keithley Model 160 digital multimeter. Samples of Al 1199 (99.994 % Al) were cut into circular samples for electrodes with an area of  $0.637 \text{ cm}^2$  when mounted in a special Teflon electrode mount (17). The samples were first metallographically polished using  $3\mu$  and  $0.3\mu$  alumina and then cleaned by conventional procedures.

In a typical experiment the sample was held potentiostatically in the passive range for 7 min and then a known volume of a solution of an aggressive anion was injected rapidly into the cell with an all

glass syringe. The time required for the current to rise sharply was measured as the induction time.

A number of solutions were analyzed for soluble aluminum. This was done by the atomic absorption spectroscopy method (18). An aluminum lamp (wavelength = 309.3nm) was used. A sample volume of about 5  $\mu\text{l}$  was usually employed. The sensitivity of the method is  $\pm 10^{-2} \mu\text{g/ml}$ .

Supporting electrolyte solutions of KH tartrate were used to measure stoichiometric numbers in the pH 3-4 range.

## Results

### Statistical treatment of data

The scatter of the measured induction times in a typical experiment is illustrated by the histogram shown on Figure 1. The statistical nature of the pitting initiation process, i.e., the induction time measured, is not due to instrumental errors of measurements, but to the inherently irreproducible character of the phenomenon under study. In such a situation Evans (19) suggested that the mode (the value obtained more frequently than any other) has greater significance than the mean since there is no reason to regard the mean (average) value as more accurate than any other. However, since the distribution plot is nearly symmetrical, it is found that the mode, the summit point of the distribution plot, coincides with the mean. Therefore, it is suggested that the use of the mean value is appropriate in the present case.

### Dependence of Induction Time on Applied Potential

The anodic polarization curve for type 1199 Al in 1N  $\text{H}_2\text{SO}_4$  shows a rise in current density at the normal corrosion potential and a slow linear increase out to 2.0 V (NHE). Potentials were selected from this range to test the dependence of the induction time on the applied potential, i.e., the potential at which the sample is held within the passive range before injection of the aggressive anion solution. Induction times were measured at 25°C, 50°C and 66°C and it was found that

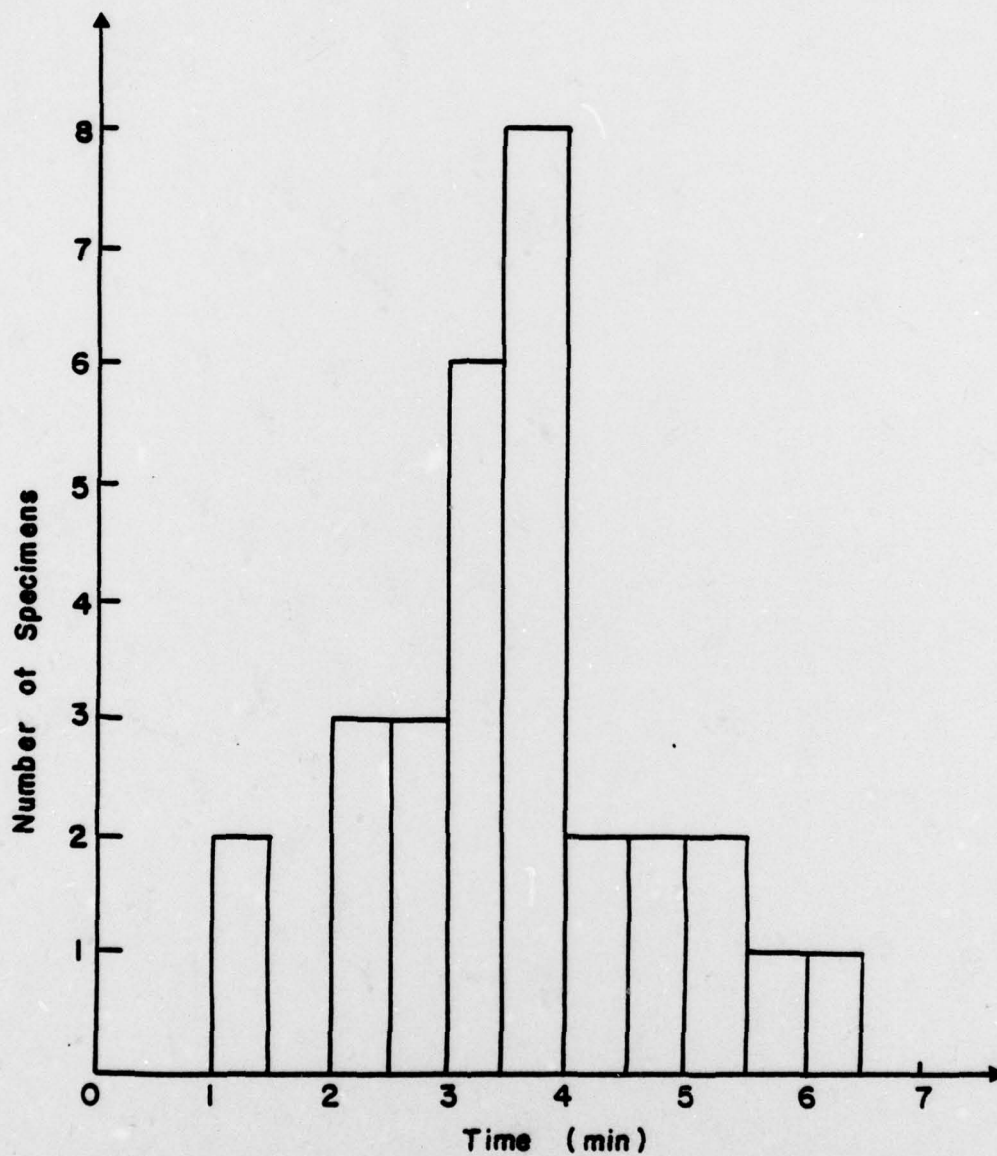


Fig.1 Histogram of induction time for 30 samples.  
Supporting electrolyte, 1N  $\text{H}_2\text{SO}_4$ ,  $[\text{Cr}] = 5.35 \text{ mM}$ ,  
Temperature  $50^\circ \text{C}$ ,  $E_{\text{applied}} = 1.25 \text{ V vs Hg/Hg}_2\text{SO}_4$

the induction time,  $\tau$ , varied linearly with the potential applied ( $E_{\text{appl.}}$ ) in the passive range. The data given in Figure 2 were taken from experiments wherein the electrodes were potentiostated near the critical pitting potential. In Figures 3 and 4 the samples were potentiostated at higher potentials still in the passive range, at 25°C and 50°C respectively. In these experiments the electrodes were held for a standard 7 minutes at the selected potential before injection of the aggressive anion solution. The scatter of the data as shown in these figures is always greater at 25°C than at higher temperatures.

It is known that when Al is anodized, the surface oxide film grows (20) and the type of anodic film formed depends mostly on the nature of the electrolyte. Porous films are formed in acid solutions such as those of sulfuric and oxalic acid while barrier type films are grown in nearly neutral solutions such as those of ammonium borate or tartrate. For porous anodic films the film thickness attainable is dependent upon the current density and time. Therefore, the act of holding the Al electrode potentiostatically in the passive range during which time a "back-ground" current flows through the specimen, contributes to the build-up of an oxide film layer. The build-up of this anodized film is directly proportional to the current density and time (21). Moreover, since the current density, the "back-ground" current, is itself linearly dependent on the applied potential in the range studied (fig. 5) it follows that the induction time is directly proportional to the thickness of the film formed. This is exactly the observation made by Foroulis and Thubrikar (12) who reported a linear dependence of induction time for pit nucleation on oxide film thickness in 0.1 M and 3 M KCl at 25°C. (Figure 5 in reference 12.)

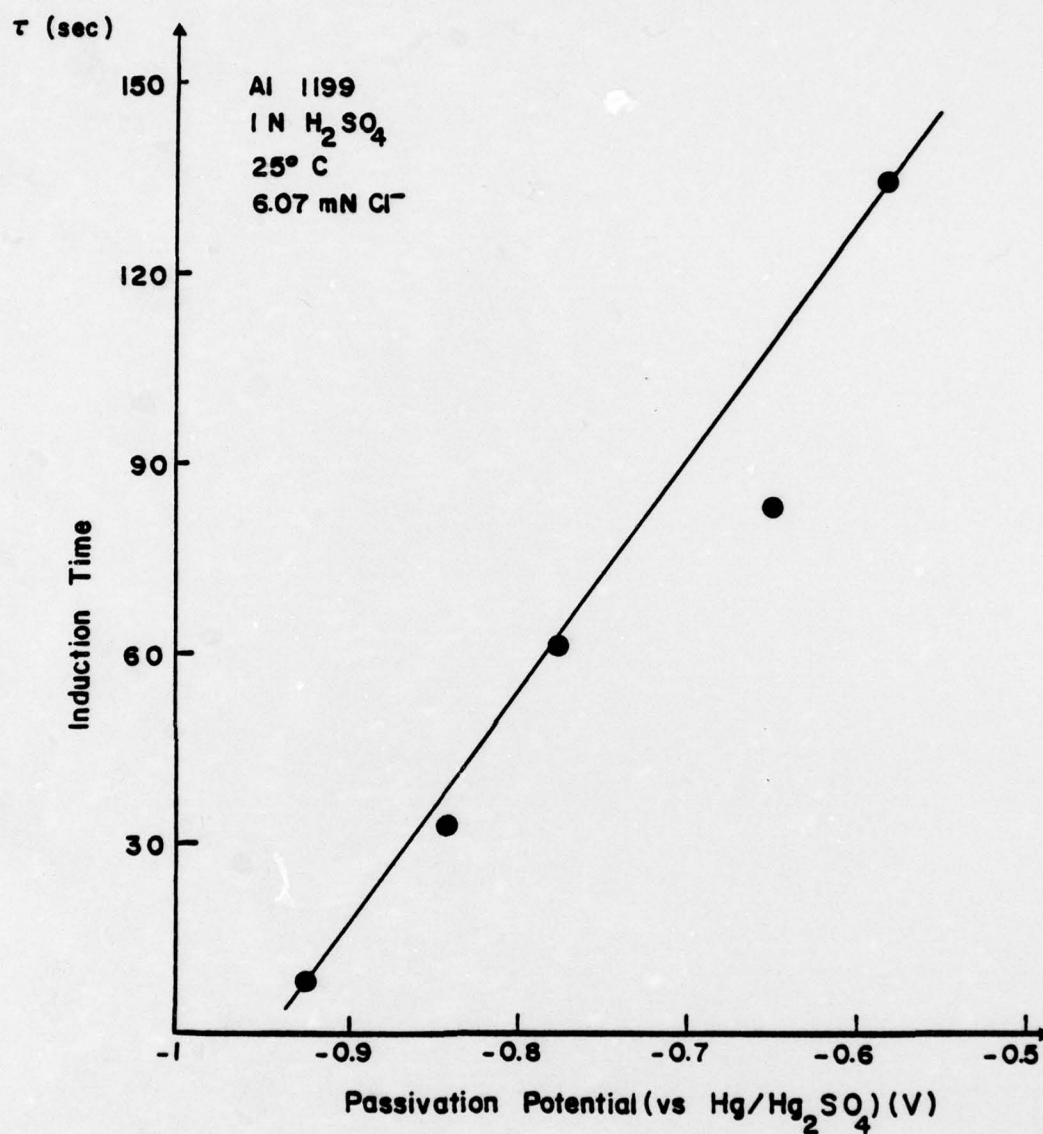


Figure 2. Dependence of induction time on passivation potential near critical potential; Al 1199; 1 N  $H_2SO_4$ ; 25°C,  $[Cl^-] = 6.07$  m N

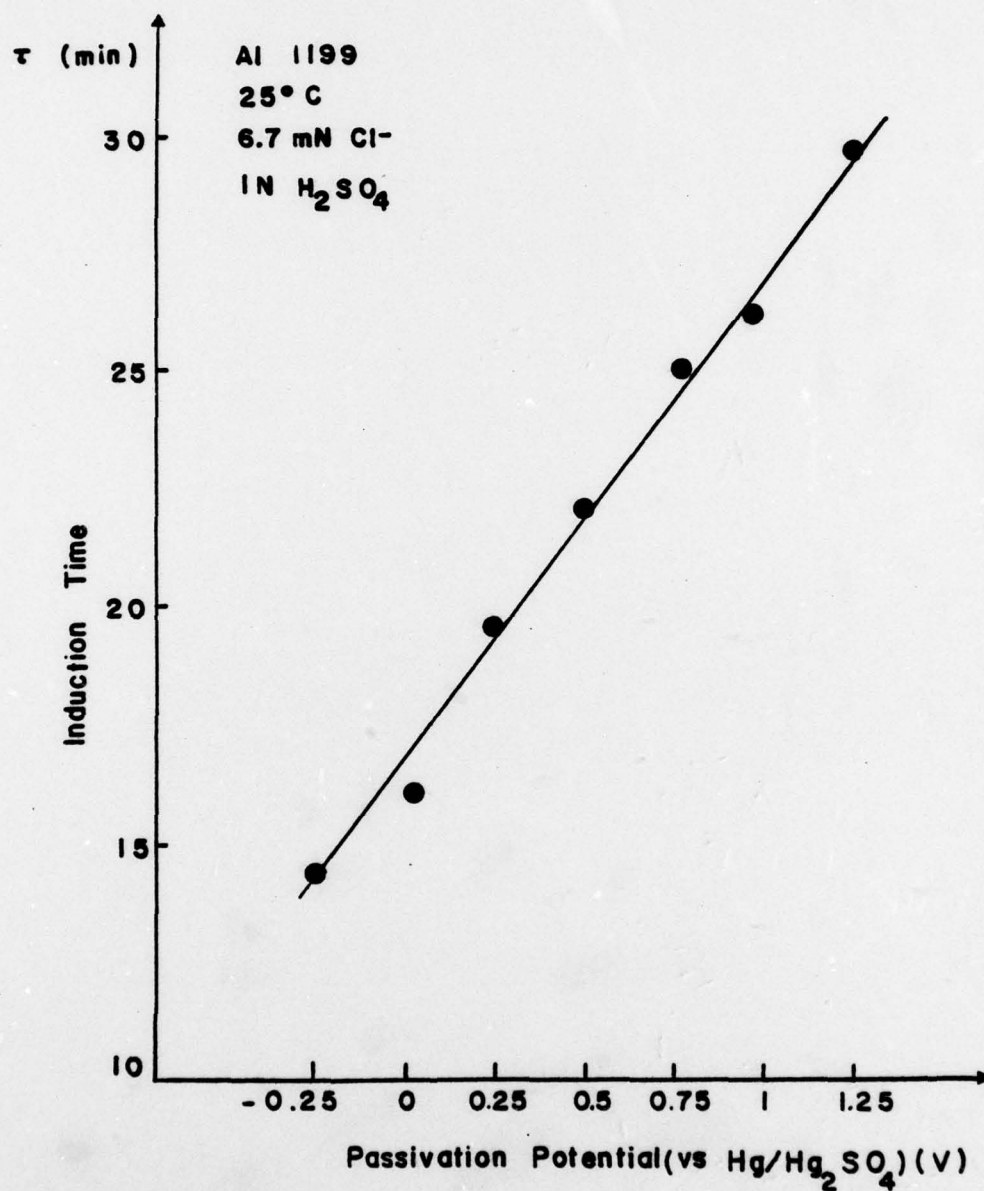


Figure 3. Dependence of induction time on passivation potential at high potentials; Al 1199; 1 N H<sub>2</sub>SO<sub>4</sub>; 25°C; [Cl<sup>-</sup>] = 6.7 m N

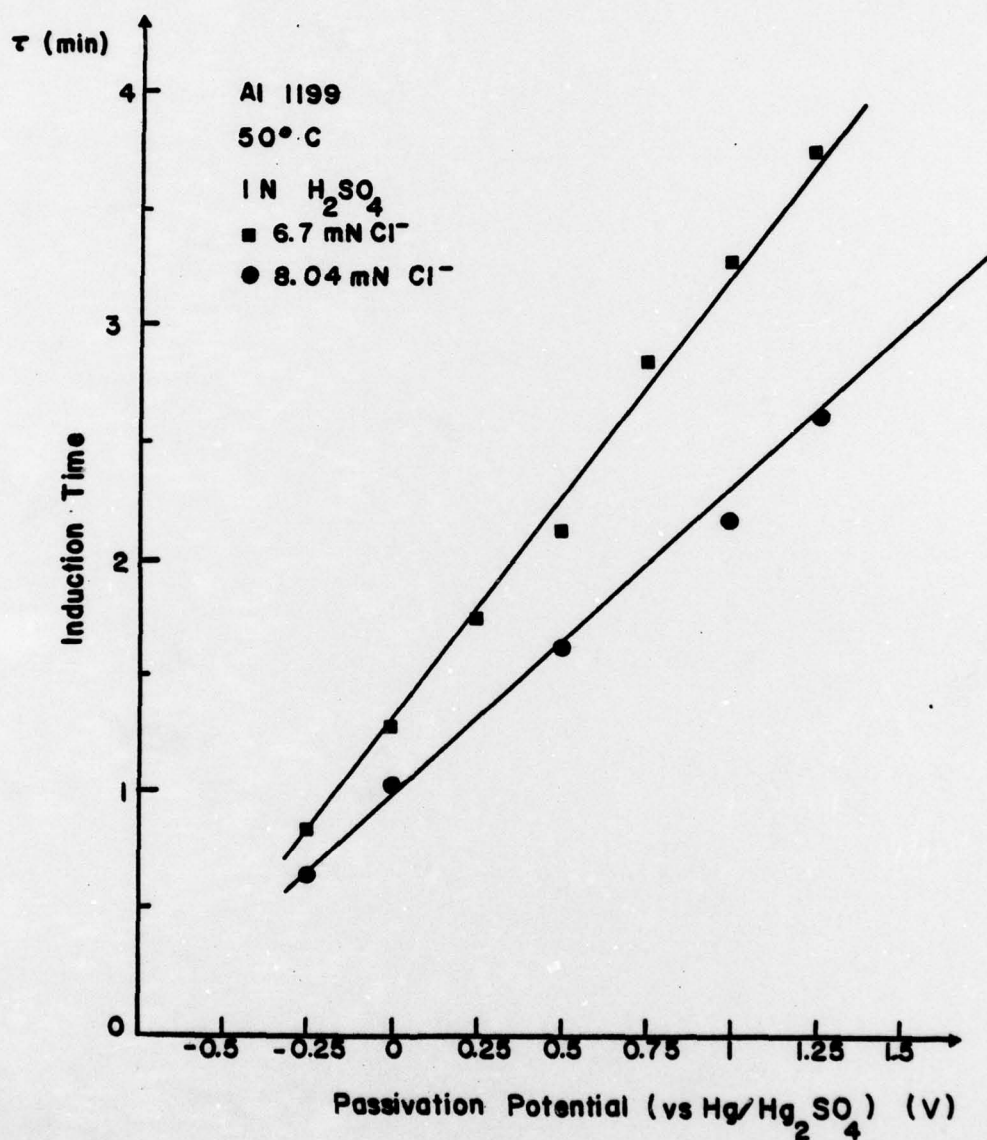


Figure 4. Dependence of induction time on passivation potential at high potentials; Al 1199; 1 N  $H_2SO_4$ ; 50°C;  
 ■  $[Cl^-] = 6.7 \text{ mN}$ ; ●  $[Cl^-] = 8.04 \text{ mN}$

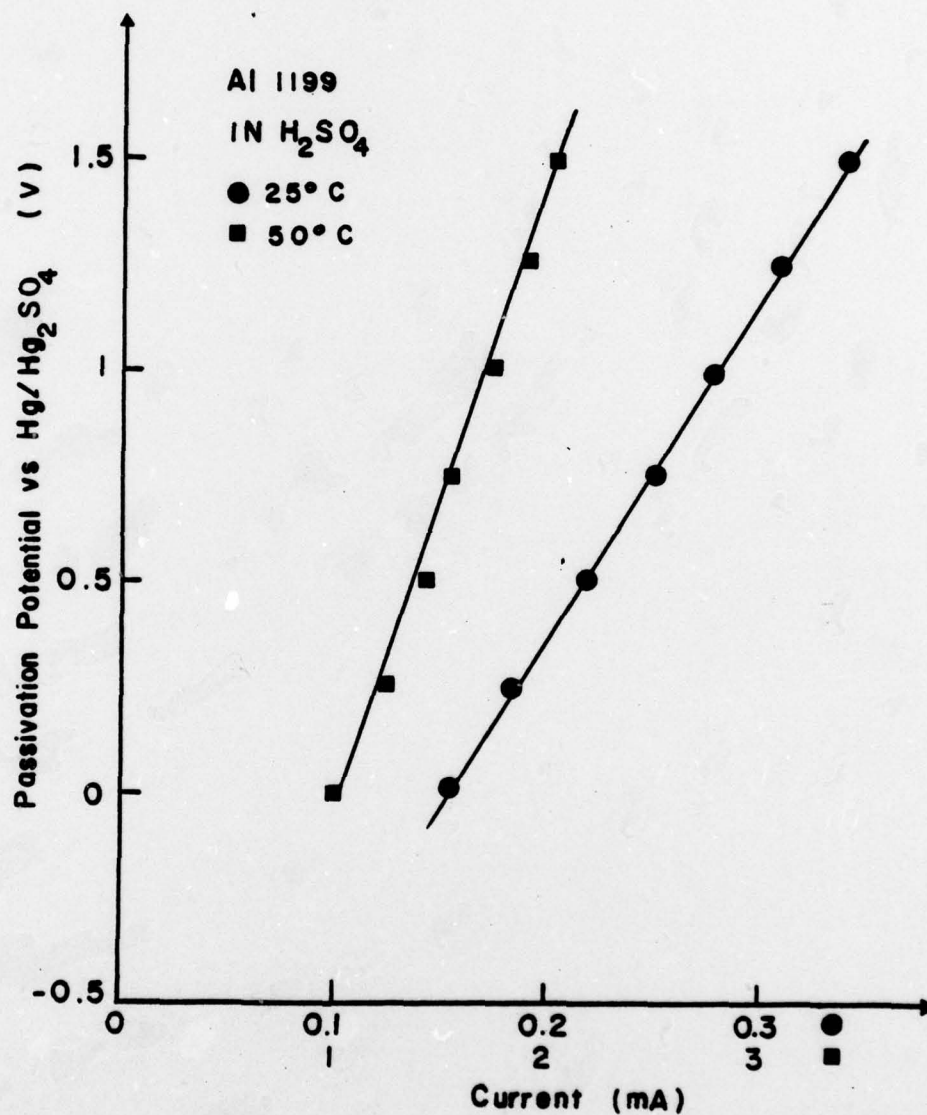


Figure 5. "Background current" as a function of passivation potential; Al 1199; 1 N  $H_2SO_4$ ; ● , 25°C; ■ , 50°C

At higher temperatures, 50°C and 66°C, the anodization process in terms of oxide film formation is less efficient than at 25°C. From Figure 5 the current at 50° is found to be 10 times higher than that at 25°C. This is due to the fact that at high temperatures, the porous film is thin, soft and nonprotective; under such conditions the process of electropolishing is achieved, i.e., where the oxide film is dissolved by the electrolyte almost as soon as it is formed. The determination of the amount of  $\text{Al}^{3+}$  dissolved into the bulk solution by the atomic absorption spectroscopy method has revealed that almost 70% of the total charge flowing through the electrode contributed to the dissolution current of Al (Table I).

From these experiments it is concluded that the pitting initiation time is potential dependent only insofar as the potential causes current to flow to build up a thicker film. Or, the pitting initiation is potential independent in the electrochemical sense. Further experimental evidence for this independency is revealed by the fact that, given equivalent amounts of charge for the build-up of the oxide layer at different potentials, the induction time is always the same (Table II).

Videm (8) viewed the same phenomena in a slightly different way. At a certain potential the electric field across the sample is

$$E = \frac{V - V_0}{x}$$

where V is the potential on the hydrogen scale and  $V_0$  has been determined to be - 1.3V. X is the thickness of the oxide layer, determined, say, by a capacitance measurement. According to Videm it is the

Table I. Efficiency of Pre-anodization Process at 50°C

$t_{\text{preanod.}}$ (min)	$Q_{\text{total}}$ (amp. sec)	$C_{\text{Al+++}}$ ( $\mu\text{g/ml}$ )	$Q_{\text{Al+++}}$ (amp. sec)	$\frac{Q_{\text{Al+++}}}{Q_{\text{total}}} \%$
40	4.56	1.83	2.94	64.4
60	6.84	3.16	5.08	74.2
86	9.83	4.75	7.64	77.9
150	17.1	8.80	14.00	81.8

\*  $E_{\text{app}} = 1.25 \text{ V vs Hg/Hg}_2\text{SO}_4$

$I_{\text{Steady State}} = 1.90 \text{ mA}$

$t_{\text{preanod.}}$ (min)	$Q_{\text{total}}$ (amp. sec)	$C_{\text{Al+++}}$ ( $\mu\text{g/ml}$ )	$Q_{\text{Al+++}}$ (amp. sec)	$\frac{Q_{\text{Al+++}}}{Q_{\text{total}}} \%$
36	3.02	1.21	1.94	64.1
85	7.14	2.86	4.60	64.4
105	8.82	3.78	6.08	68.9
190	15.96	6.90	11.19	70.1

\*  $E_{\text{app}} = 0.5 \text{ V vs Hg/Hg}_2\text{SO}_4$

$I_{\text{ss}} = 1.40 \text{ mA}$

Table II. Normalization of Induction Time for Equivalent  
Charge. Al 1199,  $\text{INH}_2\text{SO}_4$ ,  $6.7 \times 10^{-3} \text{ N Cl}^-$ ,  $25^\circ\text{C}$

$E_p \text{ (v)}$ vs $\text{Hg/Hg}_2\text{SO}_4$	$t_{\text{preanodized}}$	$i \text{ (}\mu\text{amp)}$	$Q \text{ (coulombs)}$	$\tau \text{ (min)}$
0.25	15 min	210	$3.74 \times 10^{-2}$	42 min
0.5	13 min 30 s	243	$3.73 \times 10^{-2}$	41 min
0.75	14 min 30 s	289	$4.95 \times 10^{-2}$	43 min 30 s
1.25	10 min	360	$4 \times 10^{-2}$	40 min 30s
1.5	8 min	396	$3.74 \times 10^{-2}$	42 min

electric field rather than the oxide film thickness that is the critical parameter.

On the other hand, this appears to be contrary to the observations of Nisancioglu and Holtan (22) who report that induction time decreases with increased potential and suggest that, using the method of Broli et al. (23), the critical pitting potential may be obtained by the extrapolation of a linear  $E$  vs.  $1/\gamma$  plot to  $1/\gamma = 0$ . According to our view, an extrapolation of the  $\gamma$  vs.  $E_{\text{appl.}}$  plot to  $\gamma = 0$  would represent the potential at which Al would pit in the absence of the limiting oxide film at that specific halide concentration. This extrapolation from Figure 2 yields a potential of - 0.563 v. (SCE) which compares with the critical pitting potential of - 0.583 v. reported by Nisancioglu and Holtan (22) in their summary of a number of investigations of the critical pitting potential as a function of halide concentration.

#### Pit Morphology

The applied potential does influence the morphology of the pits that are formed. At low potential,  $E_{\text{appl.}}$  (620 mv), the pits formed are hemispherical, while at high  $E_{\text{appl.}}$  (1860 mv), the pit mouth is covered by a porous layer film with a small central orifice. It is also observed that gas bubbles out through this small orifice during the pitting process. This type of pitting behavior has also been reported for austenitic stainless steel at 860 mv (vs NHE) by Makowski and Szklarska-Smialowska (24) as well as by Rosenfeld (25).

#### Stoichiometric Number and pH

The stoichiometric number "n" was determined for pit initiation by  $\text{Cl}^-$  and  $\text{Br}^-$  at a pH of 3.56 at 25°C. In these experiments the electrode was potentiostated at +0.6 v (vs  $\text{Hg}/\text{Hg}_2\text{SO}_4$ ). These values along with previously determined "n" values are listed in Table III. It is apparent that as the pH increases the stoichiometric number for the halide ion decreases.

Table III. Stoichiometric Number, "n", for Pitting of  
Aluminum Alloys by  $\text{Cl}^-$  and  $\text{Br}^-$

Alloy	Aggressive Anion	pH	Order of reaction, "n"
Al 1199	$\text{Cl}^-$	0.00	n = 4 (ref. 11)
Al 7075	$\text{Cl}^-$	0.3	n = 4-8 (ref. 13)
Al 7075	$\text{Br}^-$	0.3	n = 4 (ref. 13)
Al 1199	$\text{Cl}^-$	3.56	n = 1.5
Al 1199	$\text{Br}^-$	3.56	n = 2.5
Al 7075	$\text{Br}^-$	5.8	n = 2 (ref. 13)
Al (99.995%)	$\text{Cl}^-$	6.0	n = 2 (ref. 8)
Al 7075	$\text{Cl}^-$	5.8	n = 2 (ref. 13)
Al 1199	$\text{Cl}^-$	5.9 - 6.1	n = ~1 (ref. 12)
Al (99.53%)	$\text{Cl}^-$	neutral	n = ~1 (ref. 26)

pH 0.00 and 0.3 obtained with  $1\text{N H}_2\text{SO}_4$ ; pH 3.56 with a saturated solution of potassium acid tartrate; pH 5.8 with  $1\text{N Na}_2\text{SO}_4$ ; pH 5.9 - 6.1 with 0.1 - 3M KCl.

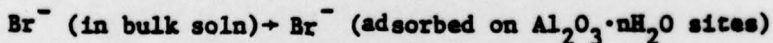
### Discussion

The breakdown of passive films by halide ions has been reviewed by Kolotyrkin (27), Hoar (28), Foley (29), and more recently by Galvele (30). From the many reports in the literature the prevalent explanations for pit initiation may be classified as follows:

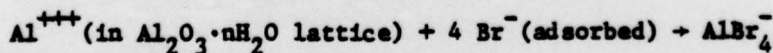
- (a) competitive adsorption, halide ions are adsorbed preferential to species such as  $\text{OH}^-$  and  $\text{H}_2\text{O}$  that would passivate the metal,
- (b) the halide ion "penetrates" the oxide film, possibly through cracks or fissures, and attacks the bare metal,
- (c) the halide ion diffuses through the oxide film (lattice diffusion) and attacks the metal,
- (d) the halide ions peptize the hydrous oxide film in the colloidal sense,
- (e) the halide ions form complexes with aluminum ions to render soluble reaction products that are normally insoluble.

As a result of the present work and other investigations previously reported it is now possible to write a mechanism in a definitive fashion.

Step 1. Adsorption on the oxide film

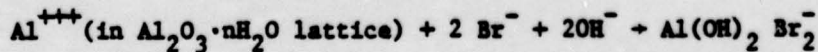


Step 2. Chemical reaction



in solutions of low pH

or



in solutions of neutral pH.

Step 3. Thinning of the oxide film.

The soluble species diffuse from the reaction site and the oxide film is thinned to the point at which aluminum ions can pass from the metal to the solution interface.

The critical step is then a chemical reaction, the formation of soluble complexes which thin the film at specific sites. For this reason the pitting of aluminum and the general corrosion of aluminum is directly dependent on the nature of the anion (7). The preferential adsorption sites may be defects or flaws in the oxide film (31).

This is essentially the mechanism proposed by Foroulis and Thubrikar (12) based on their work with pure Al in neutral solutions. They propose the formation of a soluble basic chloride salt,  $\text{Al}(\text{OH}_2)\text{Cl}$ , which, considering the intricate nature of aqueous aluminum chemistry, is as reasonable as the proposed step 2. The second step is similar to that proposed by Liepina et al. (32, 33) who viewed the process in terms of colloidal-chemical effects occurring at metal surfaces and proposed a sequence for the action of KCl on Al as  $\text{AlCl}_3 \rightarrow$  polyoxy-chloride intermediate  $\rightarrow$  amorphous gels  $\rightarrow$  boehmite  $\rightarrow$  bayerite  $\rightarrow$  hydrangellite. The mechanism also agrees with the observations of Hagyard and Santhiopillai (34) regarding the specific ability of  $\text{AlCl}_3$  solutions to activate passive aluminum.

The adsorption of halide ions on oxide-covered aluminum surfaces has been documented. Videm (8) measured the pickup of chloride-36 by autoradiography before film breakdown and during the pitting corrosion process. No pickup was detected before breakdown supporting the idea that the initial adsorbed  $\text{Cl}^-$  formed a soluble complex that

diffused out into the solution. During pitting corrosion there was heavy pickup in pits as the aluminum chlorine species was trapped in the pits with restricted diffusion. Similar results were obtained more recently by Berzins et al. (35) who measured adsorption isotherms on corroding Al with  $^{36}\text{Cl}^-$ . The adsorption was mainly localized to the corroding pit sites.

The proposal of an essentially chemical process makes the concept or existence of a critical pitting potential troublesome. However, the first adsorption step is potential dependent, not from the view of inducing a charge transfer process but rather by promoting adsorption in the oxide double layer. In such terms the critical pitting potential is that potential sufficiently negative to prevent the adsorption of halide ions. The critical potential then is dependent on the anion and this has been demonstrated by Böhni and Uhlig (36). This is also in agreement with the mechanism proposed by Stirrup et al. (37) who write the chloride dependence of the pitting potential as

$$E_p = E_p^0 + 2.3 n \frac{RT}{3F} \log_{10} [\text{Cl}^-]$$

where  $n$  is the number of  $\text{Cl}^-$  ions in the aluminum chloride complex.

In the pitting of aluminum the potential accomplishes first, the promotion of the adsorption of chloride on a purely electrostatic basis. Secondly, it promotes the formation of the oxide film and this is approximately a linear function of the potential. There is no general agreement with regard to the effect of potential on the pitting of metals other than the existence of a specific critical pitting potential for an alloy for very specific conditions of halide concentration, pH, and temperature.

An examination of the literature shows that the existence or non-existence of a potential dependence on pitting depends on the alloy system investigated and even the investigation itself. Thus, the concept of a potential-independent process of pit initiation is not new, in fact, Galvele (30) classifies depassivation processes for metals into three categories (a) electrochemical, (b) chemical, and (c)  $\text{HCl}^-$  stainless steel type with the latter being speculative as a distinct process. So-called "current-less" dissolution has been reported for Fe (38), and Fe-5Cr alloy (30) apparently related to the dissolution of ferric ion in the passive layer. The ferric ion forms several soluble complexes with  $\text{Cl}^-$ .

Brolli et al. (26) report a potential dependence in the induction time for pitting initiation of 99.53% Al and express the relationship as

$$\frac{1}{\tau} = a C_{\text{Cl}^-}^b (E - E_p)$$

As the equation suggests and from examining their data the dependence near the pitting potential in the potential range of - 600 mv to - 1010 mv (SCE) is small. At  $C_{\text{Cl}^-} = 0.003 - 0.1$  moles/l  $1/\tau$  is practically independent of potential.

The stoichiometry of the aluminum complex is, of course, pH dependent. In a number of experiments with  $\text{Cl}^-$  and  $\text{Br}^-$  the pattern emerges of a high number of halides in acid solution, e.g.,  $\text{AlBr}_4^-$ , a number of unity in neutral solutions, and an intermediate number in the pH range of 3-5. Thus the pH influences in a qualitative sense the intermediate formed during the pitting process. This agrees with previous observations made by Lorking (7) who found that the corrosion

of aluminum in the pH range of 3.0 to 13.0 is more dependent on the anion than pH. In the presence of most of the anions studied which were less polarizable than the hydroxyl anion, the anodic process is the formation of the anhydrous oxide and corrosion is controlled by the relative rates of film repair and film breakdown by chemical solution of the oxide. In the presence of chloride ions, however, the predominant anodic process is the direct solution of aluminum ions and the formation of soluble aluminum chloride instead of aluminum oxide. Or, in other words, in halide solution the formation of soluble species takes precedence over the formation of oxide.

As a general conclusion it may be stated that the findings in this study are consistent with the complex ion theory of corrosion (40). The anions function in a specific manner forming chemical species whose stabilities determine the subsequent behavior of the metal, be it accelerated dissolution or repassivation.

#### Acknowledgements

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### References

1. M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, Pergamon Press, New York (1966)
2. G. E. Thompson, R. C. Furneaux, J. A. Richardson, and J. S. Goode, Nature 272, 435 (1978)
3. J. Siejka and C. J. Ortega, J. Electrochem. Soc., 124, 883 (1977)
4. G. E. Thompson, R. C. Furneaux, G. C. Wood, and R. Hutchings, J. Electrochem. Soc., 125, 1480 (1978)
5. Ai Noguchi and N. Saito, Niigata Daigaku Kogakubu, Hokoku 24, 59 (1975)
6. K. F. Lorking and J. E. O. Mayne, J. Appl. Chem. 11, 170 (1961)
7. K. F. Lorking, Australian Defence Scientific Service, Aeronautical Research Laboratories, Metallurgy Note 61, February 1969.
8. K. Videm, Kjeller Report KR-149 (Institutt for Atomenergi) 1974.
9. H. J. Engell and N. D. Stolica, Z. Physik. Chem. N. F. 20, 113 (1959)
10. T. P. Hoar and W. R. Jacob, Nature 216, 1299 (1967)
11. F. D. Bogar and R. T. Foley, J. Electrochem. Soc. 119, 462 (1972)
12. Z. A. Foroulis and M. J. Thubrikar, J. Electrochem. Soc. 122, 1296 (1975)
13. S. Dallek and R. T. Foley, J. Electrochem. Soc. 123, 1775 (1976)
14. A. Broli and H. Holtan, Corrosion Science 13, 237 (1973)
15. N. Sato, J. Electrochem. Soc. 123, 1197 (1976)

16. T. Shibata and T. Takeyama, *Nature* 260, 315 (1976)
17. J. Myers, E. Gruenler, and L. Smulczenski, *Corrosion* 24, 352 (1968)
18. J. P. Matousek, *Amer. Lab.*, June, 45 (1971)
19. U. R. Evans, "Corrosion and Oxidation of Metals," Edward Arnold Ltd., London (1968)
20. J. W. Diggle, T. C. Downie, and C. W. Goulding, *Chem. Rev.* 69, 365 (1969)
21. F. Liechti and W. D. Treadwell, *Helv. Chem. Acta* 30, 1204 (1947)
22. K. Nisancioglu and H. Holtan, *Corrosion Science* 18, 835 (1978)
23. A. Broli, H. Holtan, and M. Midjo, *Br. Corrosion J.* 8, 174 (1973)
24. J. Makowski and Z. Szklarska-Smialowska, *Corrosion Sci.* 15, 493 (1975)
25. I. L. Rosenfeld and I. S. Danilov, *Proceeding of 3<sup>rd</sup> Int. Congr. on Metallic Corrosion*, Vol. I, Moscow 1969, p. 139.
26. A. Broli, H. Holtan, and H. Sigurdsson, *Werkstoffe und Korrosion* 26, 629 (1975)
27. Ya. M. Kolotyrkin, *Corrosion* 19, 261 (1963)
28. T. P. Hoar, *Corrosion Sci.* 7, 341 (1967)
29. R. T. Foley, *Corrosion* 26, 58 (1970)
30. J. Galvele, *Fourth Int. Symposium on Passivity* Oct. 17-21, Airlie, Virginia, U.S.A. (1977)
31. J. A. Richardson and G. C. Wood, *Corrosion Sci.* 10, 313 (1970)
32. L. Liepina and Z. Osis, *Latvijas PSR Zinātņu Akad. Vestis*, No. 6 (Whole No. 35), 35 (1950)
33. L. Liepina, A. Vaivade, Z. Osis, and A. Striprais, *Latvijas PSR Zinātņu Akad. Vestis*, No. 3 (Whole No. 8), 107 (1954)

34. T. Hagyard and J. R. Santhiopillai, J. Appl. Chem. (London) 9, 323 (1959)
35. A. Berzins, R. T. Lowson, and K. J. Mirams, Aust. J. Chem. 30, 1891 (1977)
36. H. Böhni and H. H. Uhlig, J. Electrochem. Soc. 116, 906 (1969)
37. B. N. Stirrup, N. A. Hampson, and I. S. Midgley, J. Applied Electrochemistry 5, 229 (1975)
38. K. E. Heusler and L. Fischer, Werkstoffe und Korrosion 27, 551, 697 (1976)
39. K. E. Heusler and L. Fischer, Werkstoffe und Korrosion 27, 788 (1976)
40. R. T. Foley, J. Electrochem. Soc. 122, 1493 (1975)

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